

## THERMAL RELATIONS OF SOLUTIONS.

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The thermal relations of solutions afford evidence of a peculiar and valuable kind about the nature of solutions. The electrical conductivity of solutions has been explained by the hypothesis that the molecules of the solute are partly dissociated into ions in the solution. When this hypothesis is further tested on the assumption that the osmotic pressure is proportional to the number of free molecules and ions in the solution, the experimental results of Dieterici, of Kahlenberg, of Jones and others show disaccord with the predictions of the hypothesis. I venture to believe that a study of the heat capacities and the heats of dilution of solutions will confirm the view that the reason for this disaccord lies in the assumed relation of the osmotic pressure to the dissociation, so that while the dissociation hypothesis is confirmed, the relation of the osmotic pressure to the dissociation is shown to be different from that which was originally assumed.

Five years ago I presented to this Society a paper in which I discussed the heat capacities of solutions. I will summarize here the principal results described in that paper, in order to render the present discussion more complete.

The heat capacity of a gram-molecular solution of an electrolyte diminishes with increasing dilution. The change in the heat capacity is directly proportional to the change in the dissociation, determined from the electrical conductivity. In most cases, at ordinary concentrations, the heat capacity of the water is diminished, and we are led to infer an interaction between the water and the molecules and ions of the solute of such a sort as to diminish the freedom of the water. A study of the constants of the formula by which the heat capacity is expressed leads to the conclusion that the heat capacity of the

water associated with the molecules of the solute is increased, while that of the water associated with the ions is diminished. A similar relation holds for the volumes of solutions of electrolytes. Since the heat capacity and the volume of a body are both quantities in their nature additive of the similar properties of the parts of the body, it is to be expected that there will be a similarity in their behavior in any complex and changing body like a solution. The relations described confirm in a striking way the correctness of the dissociation hypothesis and the general accuracy of the dissociation factors obtained from observations on electrical conductivity, while they also indicate as a necessary conclusion from the facts, that there is interaction between the solute and solvent. This general theory which was formerly based on the facts which have been described, receives, I believe, strong confirmation from the study of the heats of dilution.

When a solution containing one gram-molecule of solute is diluted by the addition of a unit volume of water, heat is either evolved or absorbed. This amount of heat is the heat of dilution. It is of course a function of the concentration. It also shows a remarkable dependence on the temperature. For example, if a solution of barium chloride containing one half gram-molecule in 50 gram-molecules of water is diluted to double its volume at 7° C. 49 gram-calories of heat are absorbed. The same dilution at 24.5° C. is accompanied by an evolution of 18.5 gram-calories. At some intermediate temperature, about 17° C., there is no heat either evolved or absorbed. In all cases the absorption of heat is greatest at the lowest temperature of observation, and diminishes as the temperature is raised, to become positive in some cases, as in the example just given, at temperatures common in an ordinary room. The greater the dilution, the lower the temperature at which the heat of dilution changes its sign.

A very simple thermodynamic argument proves that the rate of change of the heat of dilution with the temperature, for a fixed concentration, or what we may call the temperature coefficient of the heat of dilution, is equal to the negative value of the rate at which the heat capacity of the solution changes with an increase of volume of the solution. Using  $l$  to represent the heat of dilution, taken positive if heat is evolved,  $\theta$ , the absolute temperature,  $H$ , the heat

capacity of the solution and of an arbitrary amount of additional solvent, from which the solvent is taken with which the solution is diluted, and  $v$ , the volume of the solution, we find

$$\frac{dl}{d\theta} = -\frac{dH}{dv} = -a.$$

We may set  $dH/dv = a$ , a quantity independent of the temperature, because, first, Teudt has proven it to be so independent, within reasonable ranges of temperature, by direct observations, and, secondly, because the formula

$$l_1 - l_2 = -a(\theta_1 - \theta_2)$$

obtained from the differential equation on that supposition agrees with observations within the temperature ranges in which it has been tested. Treating  $a$  therefore as independent of the temperature we get

$$l = -a\theta + e,$$

in which the heat of dilution is expressed as the sum of two terms, one of which is proportional to the absolute temperature, the other independent of temperature. Such a relation could not be expected to hold for all temperatures, but within the narrow ranges open to experiment it seems to be valid. Of the two terms the first one is positive in all actual cases, for it is a general rule that the heat capacity of an electrolyte diminishes as the dilution increases. It corresponds to an evolution of heat. The second term is nearly of the same magnitude as the first, and is negative, corresponding to an absorption of heat.

From the experimental relation already described, connecting the heat capacity of the solution with the dissociation, it follows that the quantity  $a$  is equal to a negative constant multiplied by the rate at which the dissociation increases as the volume of solution is increased. The evolution of heat therefore which is expressed by the term  $-a\theta$  is proportional to the increase in the dissociation and to the absolute temperature. This can be explained by the theory of the constitution of a solution which has already been described. As dissociation proceeds molecules of water which have been in union

with the molecules of the solute are released and their heat capacity is diminished. At the same time molecules of water are associated with the new ions, and their heat capacity is also diminished. The act of dissociation thus diminishes the heat capacity, and therefore the number of degrees of freedom of the solution in proportion to the change of the dissociation factor, and the energy associated with those degrees of freedom, which is proportional at these temperatures to the absolute temperature, is liberated in the solution as heat. The negative term  $e$  being nearly equal at each concentration to the corresponding positive term, also varies to a first approximation with the dissociation. When calculated for the dissociation of a complete gram-molecule it is of the same order of magnitude as the heat of combination of the elements constituting the solute. It presumably contains the heat of dissociation along with the internal work done during the dilution.

The condition that  $dH/dv = a$  is independent of the temperature enables us to find a formula for the relation between the osmotic pressure and the temperature expressed in terms of the thermal constants. A thermodynamic argument shows that the osmotic pressure  $p$  satisfies the differential equation

$$\frac{d^2 p}{d\theta^2} = -\frac{a}{\theta};$$

and if  $a$  is assumed independent of  $\theta$  we integrate this equation and obtain

$$p = -a\theta(\log \theta - 1) + b\theta + e.$$

The quantities  $b$  and  $e$  are functions of the volume but are independent of the temperature.

Now by another thermodynamic argument we can deduce the heat of dilution from this value of the osmotic pressure. We obtain

$$l = -a\theta + e$$

as before, in which the function  $e$  is that which appears in the expression for the osmotic pressure. This formula can be tested by comparison with the results of experiment. From observations of the depression of the freezing point we can calculate the osmotic pressure for a fixed concentration at  $0^\circ$  C. and using this in con-

nection with the heat of dilution for the same concentration we can determine the constants of the formula. With these we can then calculate the osmotic pressure at  $100^{\circ}$  C. and compare it with the value found for this quantity from observations of the elevation of the boiling point. I was able to do this with the observations of Kahlenberg on the freezing and boiling points of sodium chloride solutions combined with those of Thomsen on the heat capacities and of myself on the heats of dilution. The agreement of the observed boiling points with those predicted from the formula was excellent. Incidentally this agreement confirms the validity of the assumption from which the formula was derived, that  $a$  is independent of the temperature.

Another test of a less searching character can be made by using the osmotic pressures given by the formula at different temperatures to calculate the ratio of the vapor pressure of the solution to that of the pure solvent. According to von Babo's law this ratio should be independent of the temperature. Calculations for sodium chloride solutions show that while it is not strictly the same at all temperatures between  $0^{\circ}$  and  $100^{\circ}$  C. yet the differences between ratios at different temperatures are excessively small, and lie within the errors of the observations by which von Babo's law has been tested.

The terms  $a$  and  $e$  of the formula for the heat of dilution are manifestly not quantities which are fundamentally kinetic in their nature. They express rates of change of energy with change of volume. Their appearance in the formula for the osmotic pressure indicates that the osmotic pressure is not to be explained as a kinetic phenomenon, as the pressure of a gas is, but as the result of forces acting between the solute—its molecules and ions—and the solvent. These thermal relations, therefore, afford strong evidence, and evidence with as little admixture of hypothesis as is possible in the nature of the case, first of the validity of the dissociation hypothesis by which the laws of electrolytic conduction are explained, and secondly, of the dependence of the osmotic pressure on the forces which are exerted between the parts of the solution and the pure solvent.